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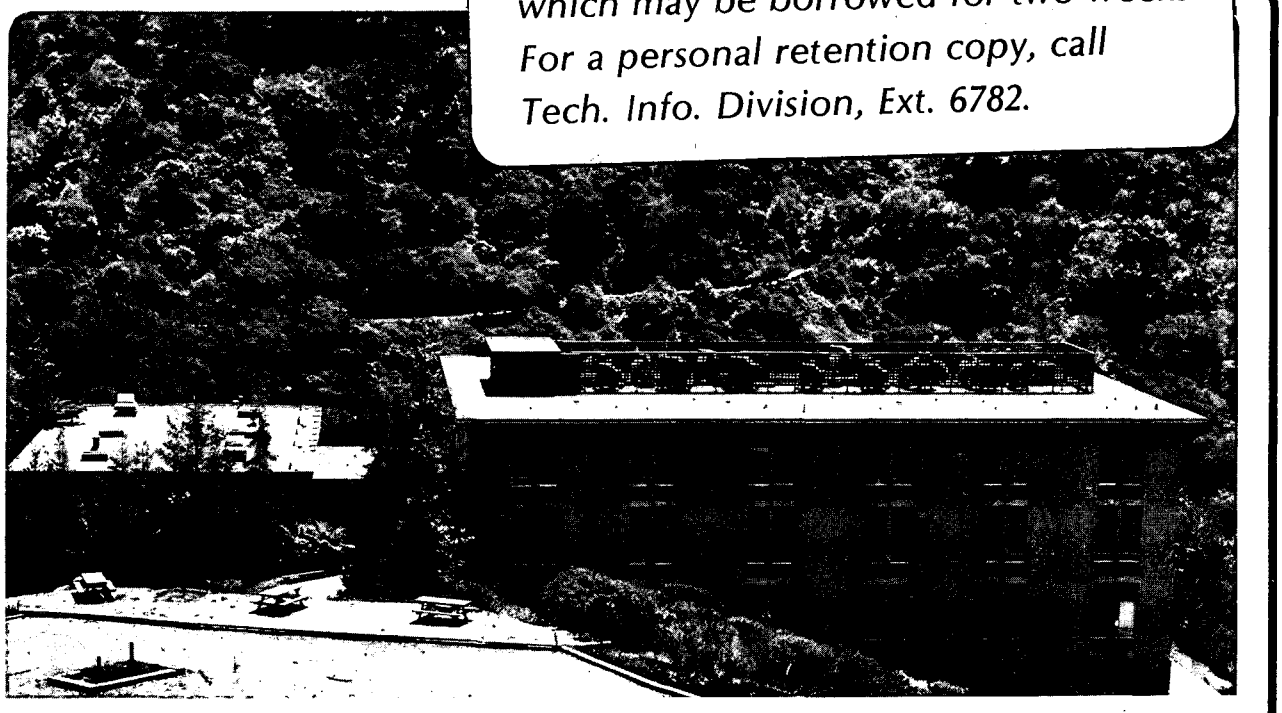

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DISCLAIMER

MODEL CALCULATION OF BINDING ENERGIES FOR MULTIHOLE COPPER CENTERS IN GERMANIUM

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Abstract

Multihole binding energies of copper centers in germanium are calculated within a pseudoatom variational scheme in which a Heine-Abarenkov-type model potential is used as the impurity potential. Screening the hole-hole interaction by a position-dependent dielectric function is found to be crucial in understanding the observed multihole binding energies.

I. INTRODUCTION

Experimental work on positively charged acceptors in high-purity germanium has recently been reported.[1,2] The experimental binding energies of the extra hole for several triply occupied, double acceptors (Be^+, Zn^+, Mg^+, Mn^+, and Hg^+) and for the overcharged triple acceptor Cu^+ in Ge were measured with photoconductive far-infrared spectroscopy. Theoretically, a simple pseudoatom variational calculation[3] clearly indicated that the extra hole is bound. Notice that in the case of acceptors in Ge, the fourfold degeneracy of the top of the valence bands makes possible the existence of the $(1s)^3$ and $(1s)^4$ configurations and one therefore can describe up to four holes with the same spatial envelope wavefunction, equivalent to hydrogenic pseudoatoms with spin-3/2 electrons. An effective Rydberg (Ry^*) is obtained[2] by fitting the theoretical prediction for the binding energy of the neutral A^0 state to the measured value. The theoretical[2,3]

binding energies for the singly ionized A^- and for the overcharged A^+ in germanium are then compared with experiment. Very good agreement, given the extreme simplicity of the variational calculation, is obtained for the double acceptors. For the copper triple acceptor, however, the same variational procedure yields the following[2,3] binding energies, $E(Cu^{--}) = 143.2$ meV, $E(Cu^-) = 87.8$ meV, $E(Cu^\circ) = 43.21$ meV (fitted) and $E(Cu^+) = 10.4$ meV to be compared with the experimental[2,4] values of 410 meV, 330 meV, 43.21 meV, and 2.0 meV, respectively. It is clear, therefore, that a better understanding of the observed multihole binding energies requires modification of the copper impurity potential to take chemical effects into account and, as we hope to demonstrate, proper consideration of the screening of the strong hole-hole interaction.

II. THE MODEL POTENTIAL AND THE HOLE-HOLE INTERACTION

In what follows we adopt, for the purpose of our calculations, the concept of pseudoatoms[1-3] which can bind up to four spin-3/2 electrons in the ground state. Thus Cu^+ is the analog of pseudo Li^-; Cu°, the analog of pseudo Li°, etc. We assume the $\underline{n}$-electron variational wavefunction to be of a multiple-exponential form[3,5]

$$\psi(\underline{r}_1,\underline{r}_2,\ldots,\underline{r}_n) = \hat{S} \exp\left(-\sum_i \alpha_i r_i\right), \qquad (2.1)$$

where $\hat{S}$ is the symmetrizing operator and the α_i $(i=1,\ldots,n)$ are

variational exponents which minimize the energy with the n-electron Hamiltonian

$$H = \sum_{i=1}^{n} \left[- \frac{\hbar^2 \nabla_i^2}{2\mu^*} + V(r_i) \right] + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{1}{\varepsilon(\underline{r}_i, \underline{r}_j)} \frac{e^2}{r_{ij}} \, . \quad (2.2)$$

The electron effective mass μ^* is expected to be position dependent.[6] For $r \rightarrow \infty$ we can take $\mu^* \sim m^*$, with $m^* = 0.17m$ the hydrogenic effective mass constant obtained previously by a variational procedure.[7] As it approaches the impurity site, the potential seen by the electron becomes different from that given by the (constant) effective mass approximation; at the origin μ^* should be just the free electron mass $\underline{m}$. We used an expression for $\mu^*(r)$ which was first proposed by Hermanson[8] and used by Jaros[9] in the treatment of shallow donors,

$$\frac{1}{\mu^*(r)} = \frac{1}{m^*} + \left(1 - \frac{1}{m^*}\right) e^{-r/r_m} \, , \quad (2.3)$$

with $r_m = 1.4$ a.u. and such that $\mu^* \sim m^*$ at the nearest neighbor distance from the impurity site.[9]

For the impurity potential we used a Heine-Abarenkov-type model potential[9,10] of the form (see Fig. 1)

$$V(r_i) = \begin{cases} A \, , & r_i < R_M \, , \\ \dfrac{-3e^2}{\varepsilon(r_i) r_i} \, , & r_i > R_M \, , \end{cases} \quad (2.4)$$

with R_M=2.0 a.u. and a variable depth A. The dielectric screening function $\varepsilon(r)$ was taken to be of the form[8]

$$\frac{1}{\varepsilon(r)} = \frac{1}{\varepsilon_o} + \left(1 - \frac{1}{\varepsilon_o}\right) e^{-r/a_o} , \qquad (2.5)$$

where ε_o=16 is the static dielectric constant for Ge and a_o=1.67 a.u. is a screening parameter.[9]

The hole-hole interaction in (2.2) was screened by a dielectric response function $\varepsilon(\underline{r}_i,\underline{r}_j)$ of the form

$$\frac{1}{\varepsilon(\underline{r}_i,\underline{r}_j)} = \frac{1}{\varepsilon_o} + \left(1 - \frac{1}{\varepsilon_o}\right) e^{-(r_i+r_j)/a} \qquad (2.6)$$

which apart from being very convenient from the calculational point of view (expectation values can be calculated analytically), has the appropriate behavior ε=1 when $r_i, r_j << a$ and reduces to $\varepsilon=\varepsilon_o$ for $r_i, r_j >> a$. We comment further on this choice for the hole-hole screening in the next section. It is worth pointing out that all necessary integrals appearing in $\langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle$ can be performed analytically and that only the minimization requires numerical handling.

III. RESULTS AND DISCUSSION

We first carried out calculations within the pseudoatom variational scheme using an impurity potential of the form (2.4) with a variable potential depth A and with a constant hole-hole

screening $\varepsilon(\underset{\sim}{r}_i,\underset{\sim}{r}_j)=\varepsilon_o$ which corresponds to take a $\rightarrow 0^+$ in (2.6). The resulting binding energies of multihole copper centers in germanium are plotted in Figure 2 as functions of the depth A of the potential well. One notices that the multihole binding energies have a very weak dependence on the potential depth up to A ~ -1.3 Ry reflecting a situation in which the hole (or holes) is mostly outside the central cell region and is essentially insensitive to changes of the potential near the impurity site. For large negative values of $A \lesssim -1.3$ Ry, the hole (or holes) is more and more localized around the impurity site and small changes in the impurity potential around the central-cell region have large effects on the multihole binding energies. In order to investigate the importance of the hole-hole interaction we performed calculations with the hole-hole screening $\varepsilon(\underset{\sim}{r}_i,\underset{\sim}{r}_j)$ given by (2.6) with a variable screening parameter a, and with a fixed impurity potential depth A = -1.77 Ry (see Figure 1) in such a way that the theoretical prediction for the binding energy of the single hole Cu^{--} state gives the measured[4] value $E(Cu^{--})=410$ meV. Figure 3 displays the dependence of the binding energies of Cu^-, Cu^o and Cu^+ centers on the hole-hole screening parameter a. Notice that the theoretical variational binding energies of multihole copper centers in Ge depend dramatically on the hole-hole screening with variations from about 300 meV

(for a~0) to about 2 meV (for a~10 a.u.) in the case of the positively charged (four holes) Cu^+ center [$E_{exp}(Cu^+)$=2 meV]. In conclusion, we believe that our simple model calculation demonstrates that a better theoretical understanding of the experimental multihole binding energies of copper centers in Ge must take into account not only modifications of the copper impurity potential in the central-cell region, but must also include a position-dependent screening of the strong hole-hole interaction.

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6. For a position dependent $\mu^*(r)$, the operator $p^2/2\mu^*$ is replaced by the hermitian symmetric form

$$\frac{1}{4}\left(\frac{1}{\mu^*(r)}\,p^2 + p^2\,\frac{1}{\mu^*(r)}\right).$$

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FIGURE CAPTIONS

Figure 1. Model potential used in the calculations.

Figure 2. Multihole binding energies of copper centers in germanium as functions of the depth of the potential well. The hole-hole screening is kept constant. The arrows on the right indicate the experimental binding energies.

Figure 3. Multihole binding energies of copper centers in germanium as functions of the hole-hole screening parameter $\underline{a}$. The arrows on the right indicate the experimental binding energies. The upper horizontal scale gives $\underline{a}$ in units of the impurity-hole screening parameter $\underline{a}_0$, see Eq. (2.5).

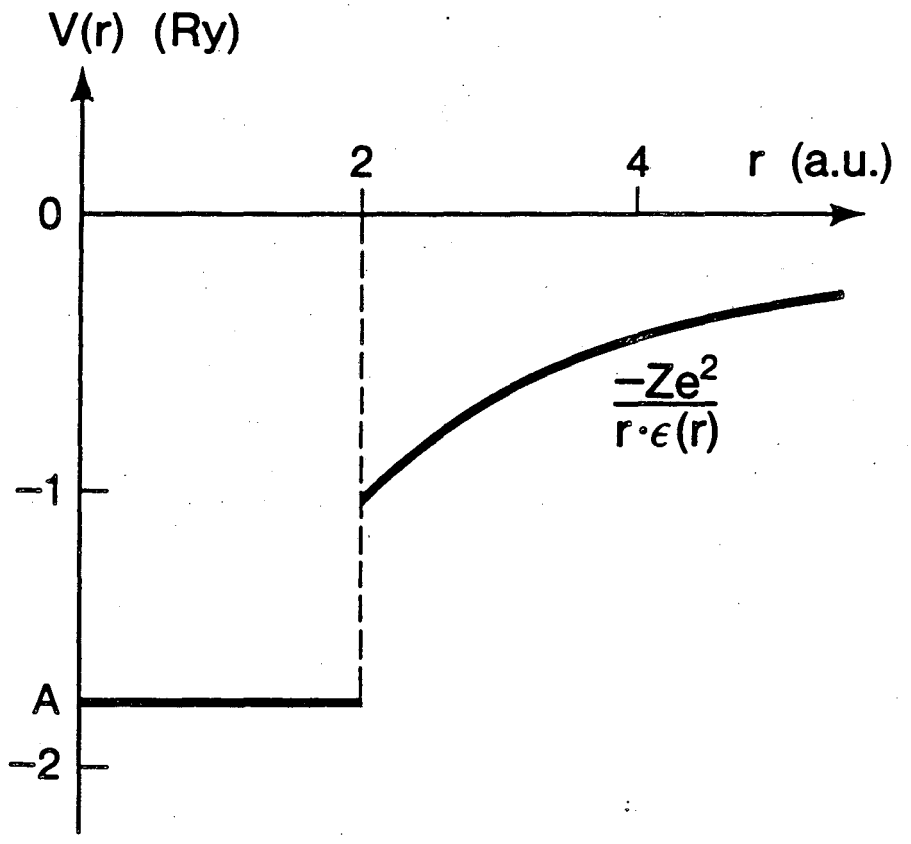

Figure 1

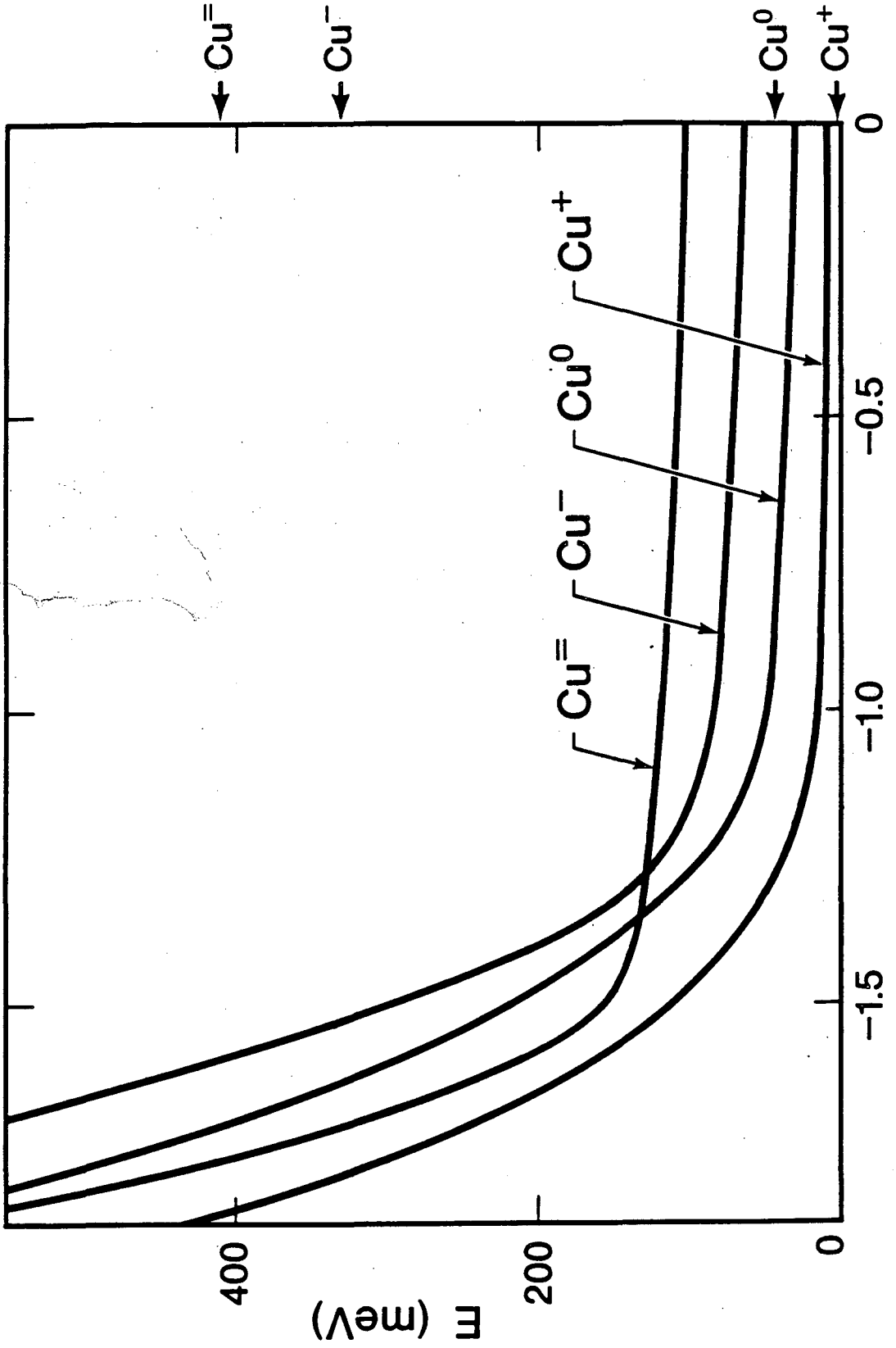

Figure 2

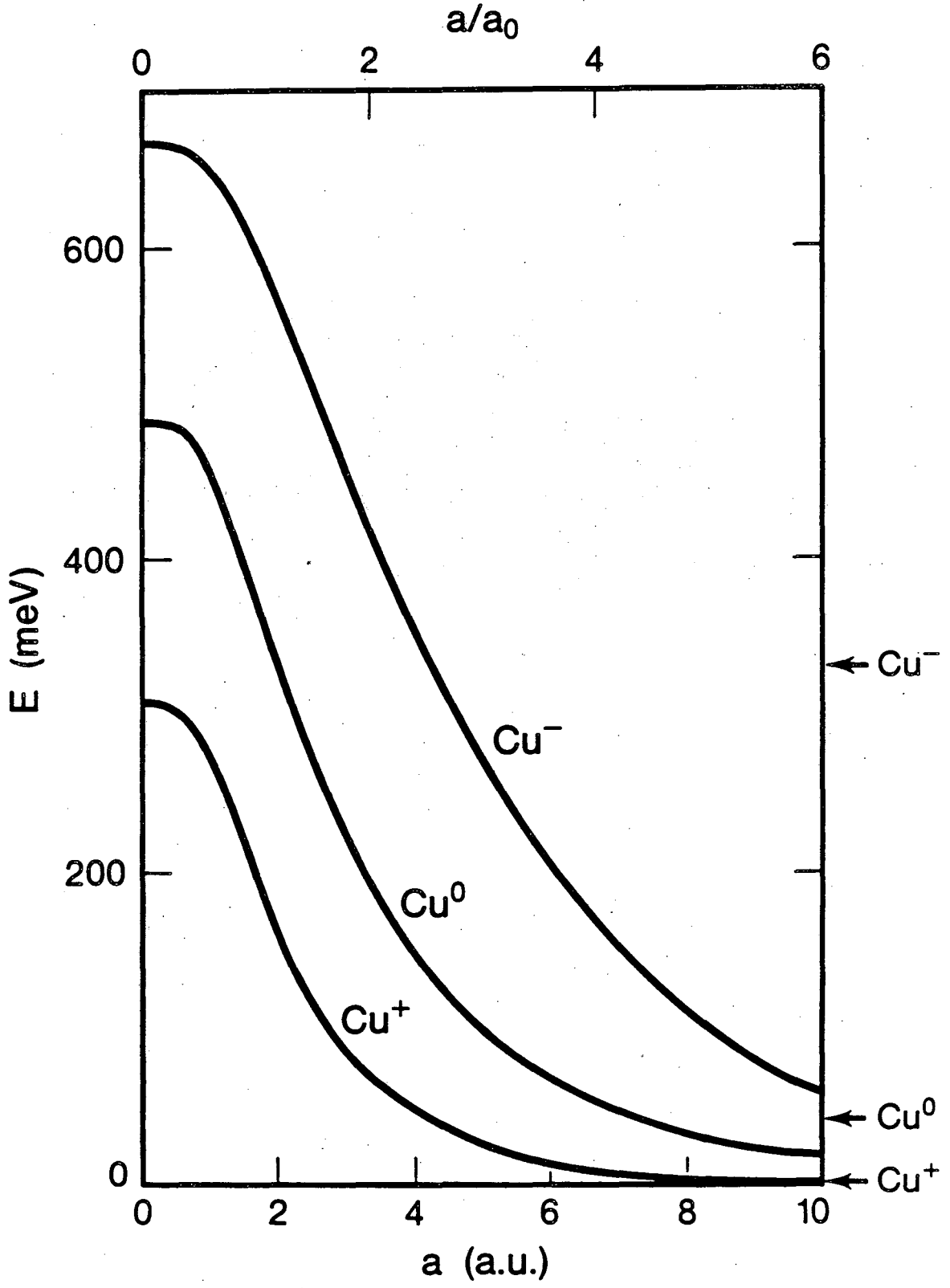

Figure 3

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